

# Liquid phase exfoliation of graphite, multiwalled carbon nanotubes and graphite-bioglass suspension

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**Abstract.** Carbon allotropes such as graphene and multiwalled carbon nanotube (MWCNT) are studied for extensive range of applications, in which various exfoliation techniques were employed to yield the best form of generated allotropes. Liquid phase exfoliation utilizes the technique of sonication of these allotropes in solvent, results in best desired form of high quality, safe, simple and economically viable final product. This study discusses on liquid phase exfoliation of graphene and MWCNT in chloroform, where their absorbance intensity shown a contrast solubility profile with respect to different weight percentages of each allotropes. The comparative study was further analysed with modification of BG within the suspensions, of which hazards in agglomerations of allotropes' particles as concentration increases could potentially give a prevention insight for a better preparation and processing of materials formulation. Hence the study aims in reporting absorbance intensity via UV-Vis of a range of weight percentages of liquid exfoliated graphene and MWCNT particles, with addition of BG, in chloroform and their exploitation in diverse potential applications including biomedical engineering field.

**Keywords:** Graphene, MWCNT, Bioglass

## 1 Introduction

Graphene, known to be a wonder material, made its experimental breakthrough in 2004 via micromechanical exfoliation from graphite, comprises of  $sp^2$  bonded carbon atoms arranged in a honeycomb lattice two-dimensional (2D) single layer. Knowing to exhibit various and distinct mechanical, physical, electrical and thermal properties, graphene

has been extensively studied in a number of applications in its early research stage including supercapacitors, energy storage, sensors and nanocomposites [1][2]. Graphene compiles and demonstrates unique properties by having high surface area, high Young's modulus, excellent thermal and electrical characteristics and also distinct optical properties which makes the material attractive for exploitation in the biomedical field. Current and ongoing research on utilising graphene and its derivatives range from drug delivery, biosensing to the development of biomedical devices for healthcare engineering applications [3][4][5].

To date, various techniques have been employed to generate graphene. Importantly, considering the dynamic and detailed development of the various industries, significant efforts were devoted to ensure a reproducible, non-structural defective and high-quality material could be obtained. In brief, preparation of graphene can be categorised as either a "bottom-up", or a "top-down" approach. The former category can be further divided into examples such as epitaxial growth and chemical vapor deposition (CVD), which enable production of large size graphene. However, these approaches display some drawbacks in producing limited dimensions and utilise very high working temperatures, hence hindering the production of high-quality graphene that is usually economically viable [6]. Meanwhile, examples of top-down approaches such as pioneers mechanical cleavage and the Hummers' method are much more desirable as they are able to yield graphene at reasonably low cost: however, both methods suffer from low-scale production and generate graphene with structural defects [6][7]. As such, a more reliable top-down method to produce graphene- via liquid phase exfoliation- has gained significant interest as it is not only able to produce high-quality graphene but is also simple, safe, and economically viable [1][8].

Liquid phase exfoliation of graphene is the action of utilising sonication in exfoliating a monolayer or a few-layer defect-free graphene from graphite in solvent. The mechanism is purposely to detach the Van der Waals forces between graphene layers, within graphite, via propagation of cavitation bubbles from ultrasonic waves through the medium which induces physical or chemical surface tension within the molecules between the solvent and the forces [6][1]. There are various solvents studied in exfoliating graphene via liquid phase exfoliation with the majority having a surface tension value around 40-50 mJ/m<sup>2</sup> [9]. Some of the most commonly used solvents include DMF (N,N)-Dimethylformamide), ODCB (ortho-dichlorobenzene), and chloroform. Each solvent requires a different sonication period which consequently generates graphene at different concentrations [9].

Meanwhile another form of carbon allotrope, multiwalled carbon nanotubes (MWCNTs), has also gained a lot of interest within the research environment due to its optical, mechanical and electrical properties. MWCNTs are essentially rolled graphene sheets which allures to it having similar characteristics to graphene. However, due to the high aspect ratio and stronger  $\pi$ - $\pi$  interactions between the tubes, MWCNTs are hindered by their solubility in organic and aqueous solvents which lead to the consequent aggregation in these media and also difficulties in large-scale processing and manufacture [10][11]. As such, the functionalisation of these carbon allotropes is one

of the most studied area in order to improve their native solubility as well as contributing to the overall characteristics of composites- especially for novel applications such as biomedical and healthcare engineering.

On the other hand, bioactive glass (BG) is a type of bio-ceramics which exhibits biocompatibility, biodegradability and excellent bioactivity, antibacterial and anti-inflammatory properties [12]. This material is also able to form an apatite layer on its surface upon contact with physiological fluid which subsequently induce angiogenesis [13]. The exploitation and modification of BG has always been the subject of interest due to the natural brittleness of BG's structure- where its distinct features to support and improve cells adhesion either by itself or when being incorporated into biomaterials offers a great deal of potential to many applications.

Therefore, this study reports in detail, the generation of graphene via liquid phase exfoliation in chloroform with respect to the different weight percentage of graphite powder, alongside an additional comparative study against MWCNT. Subsequently, this present study will provide a comparative insight on the absorbance intensity, via UV-Vis analyses, between graphene and MWCNT. In addition, functionalisation of the material with BG suspension in chloroform will be assessed and may allow its exploitation in a wide range of diverse applications that include materials science, drug delivery and tissue engineering.

## **2 Materials and Methods**

### **2.1 Materials**

Graphite powder (Cat. No: 104206, Supelco, Merck KGaA, Darmstadt, Germany), multiwalled carbon nanotubes (MWCNTs) (UN19FMW011, Nano Malaysia, USM), 45S5 bioactive glass powder (BG) was synthesised as previously reported [14], chloroform (Sigma Aldrich, Malaysia).

### **2.2 Exfoliation of graphene**

Liquid exfoliation of graphene was performed in chloroform containing graphite powder in weight percentages (wt.%) from 1.56, 3.125, 6.25 and 12.5 wt.%. The solutions were then subjected to sonication using a table top sonicator at room temperature (Bandelin, Sonorex) for 120 min, subsequently followed by centrifuge (Eppendorf 5810R, Germany) at 4000 rpm for 30 min [6]. Chloroform without graphite powder was used as control.

### **2.3 Exfoliation of multiwalled carbon nanotubes (MWCNTs)**

Similarly to graphene, MWCNTs were prepared via liquid exfoliation in chloroform with different wt.% of 1.56, 3.125, 6.25 and 12.5 wt.%. Based on a previous study, MWCNTs require shorter sonication time of around 10 min [15] before being centrifuged at 4000 rpm for 30 min.

## 2.4 Preparation of BG suspension

BG powder (BG) was prepared according to previous published paper [14]. The powder was dissolved in chloroform at different wt.% of 1, 5, 10, 20 and 30 wt.%. In order to obtain homogenous solution, the mixtures were dispersed via sonication for 120 min before being centrifuged at 4000 rpm for 30 min.

## 2.5 Preparation of graphene/BG and MWCNT/BG suspension

Both graphite (G) and MWCNT powder (3 wt% and 6 wt%) was combined with BG powder (1% and 2.5 wt%), with chloroform as the control. Graphite-BG (G-BG) and MWCNT-BG solutions were then subjected to liquid exfoliation by sonicating for 120 min and 10 min respectively, before both were centrifuged at 4000 rpm for 30 min.

## 2.6 Absorbance intensity study of exfoliated suspension

Absorbance intensity of exfoliated suspensions were studied and analysed via a UV-Vis spectrometer (Fluostar Omega, BMG Labtech, Germany). The intensity of the suspensions were read at wavelength between 220 nm to 800 nm, with chloroform used as the background inside a 96-well plate (Nunclon, Delta Surface, ThermoScientific) with three replicates for each samples.

## 2.7 Statistical analysis

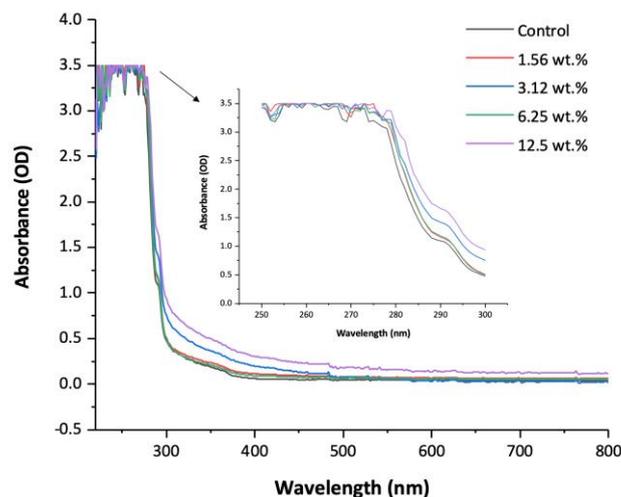
All results presented are expressed as mean values and standard deviation (Mean $\pm$ SD) of number of trials. All the data was statistically analysed via OriginLab software (Origin Lab, Northampton, USA) and SPSS Version 26 (IBM Inc, Armonk, NY, USA).

# 3 Results and Discussions

## 3.1 Exfoliation of graphene in chloroform

Figure 1 shows broad peaks of graphene intensity for different weight percentages recorded. Although more significant peaks are expected similar to other previous studies [16][17][18], however the broad peaks obtained might most likely due to batch to batch variation of the starting material and might also due to limited maximum absorbance range detected by the machine. Nonetheless, the appearance of anticipated characteristic absorption peak approximately at  $\sim$ 270 nm wavelength was seen which indicates the presence of graphene dispersion for all different weight percentages of graphite that corresponds to the restored  $\pi$ -conjugation network transition of C-O bonds of graphene [5][6]. The absorbance intensity via UV-Vis shown an increasing value as weight percentage of graphite increases, except for graphite powder at 6.25 wt.% which shown low intensity and at almost similar range of control sample, and most likely due to potential starting of agglomeration or sample error where the graphite powder was accidentally included in the well plate during reading inside the microplate reader. The general profile trend displays in the Figure 1 shown an increment in radiation being

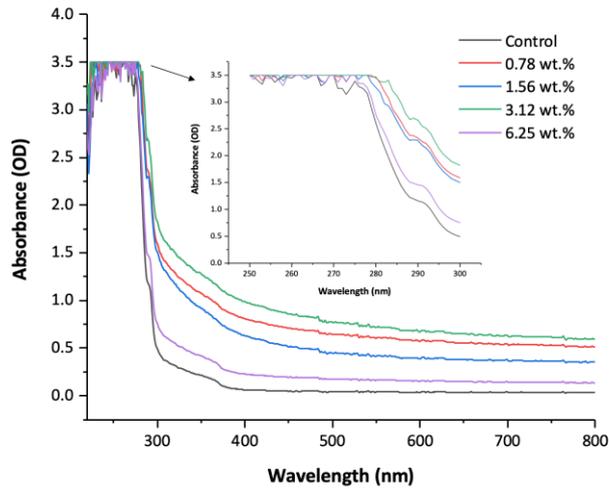
absorbed as the concentration increases, as absorbance is directly proportional to concentration.



**Fig. 1.** Absorbance intensity of different weight percentage of liquid exfoliated graphene in chloroform. Insert figure shows a clearer plateau absorption region ranging from 250-300 nm.

### 3.2 Exfoliation of multiwalled carbon nanotubes (MWCNTs) in chloroform

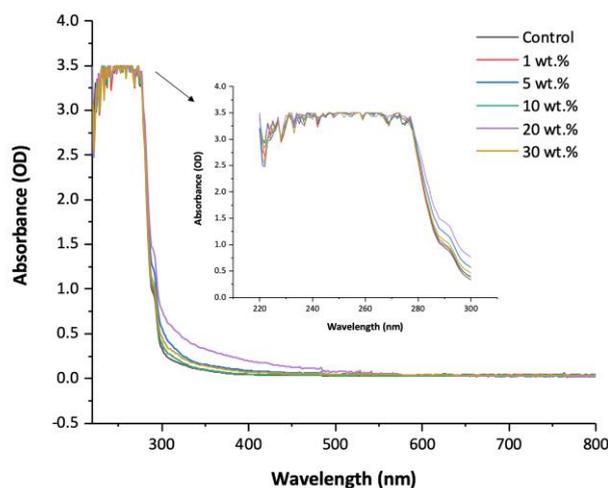
For MWCNT in chloroform, Figure 2 shows a similar broad peaks appearance, in which absorbance bands can be seen at approximately  $\sim 262$  nm which are attributed to C=C bonds and also the dispersion into individual nanotubes of MWCNTs [10]. However, the results show a contrasting trend to graphene whereby decreasing the MWCNT weight percentages result in an increase in the absorbance intensity. An exception is the 3.12 wt.% MWCNT sample in which the highest intensity is recorded for liquid exfoliation of MWCNT in chloroform. This shows that MWCNT is the most stable at 3.12 wt.% with minimal signs of agglomeration, which potentially addressed as optimised concentration of MWCNT sonicated in chloroform that exhibits the lowest Van der Waals forces between the particle and solvent which prevents the dynamic entanglement process but need further exploration since the sonication time was chosen to be within 10 minutes only. However the trend exhibited by MWCNTs show that as concentration increases, absorbance intensity decreases which indicates presence of sedimentation of large particles due to agglomeration within MWCNTs [19]. This may be attributed to the air bubbles that formed naturally by means of bridging during sonication of MWCNT that surely promotes agglomeration.



**Fig. 2.** Absorbance intensity of different weight percentage of liquid exfoliated MWCNT in chloroform. Insert figure shows a clearer plateau absorption region ranging from 250-300 nm.

### 3.3 Exfoliation of BG suspension in chloroform

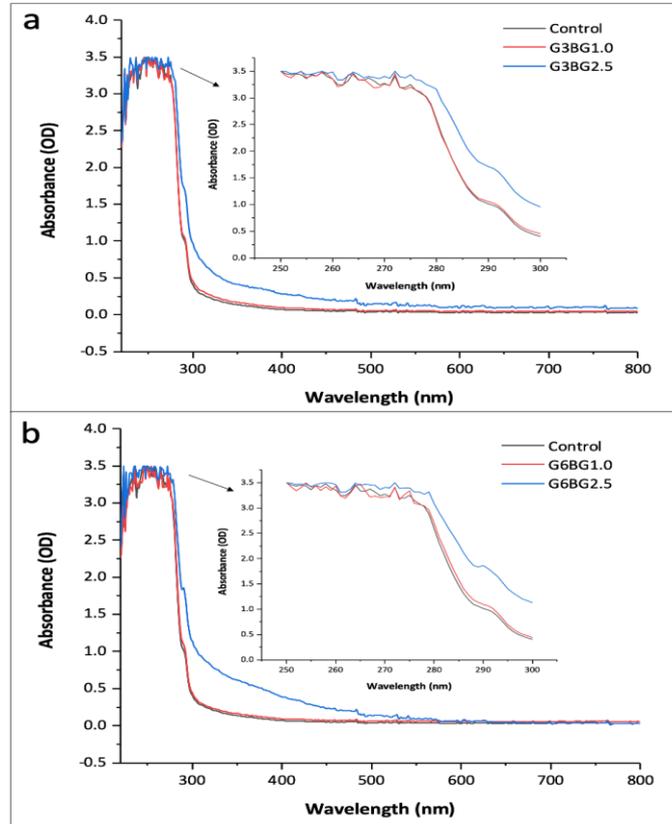
A comparative study for BG suspension in chloroform prior to addition for both graphene and MWCNT is shown in Figure 3. An extending absorption band of BG at approximately from 200-300 nm was similar to other published paper which indicates the presence of the iron impurities species  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  found in the raw materials used to prepare BG and also due to the possible presence of more than one site of both iron species which attributes to high charge transfer bands due to different absorption coefficients between both species [20]. Nonetheless, as concentration of the BG increases, the absorbance intensity increases which corresponds to the directly proportional relationship between both parameters: although at the higher concentration of BG (i.e. 30%), a drop in intensity is observed which might be due to the commencement of particle agglomeration.



**Fig. 3.** Absorbance intensity of different weight percentage of BG suspension in chloroform. Insert figure shows a clearer plateau absorption region ranging from 250-300 nm.

### 3.4 Exfoliation of graphene/BG suspension in chloroform

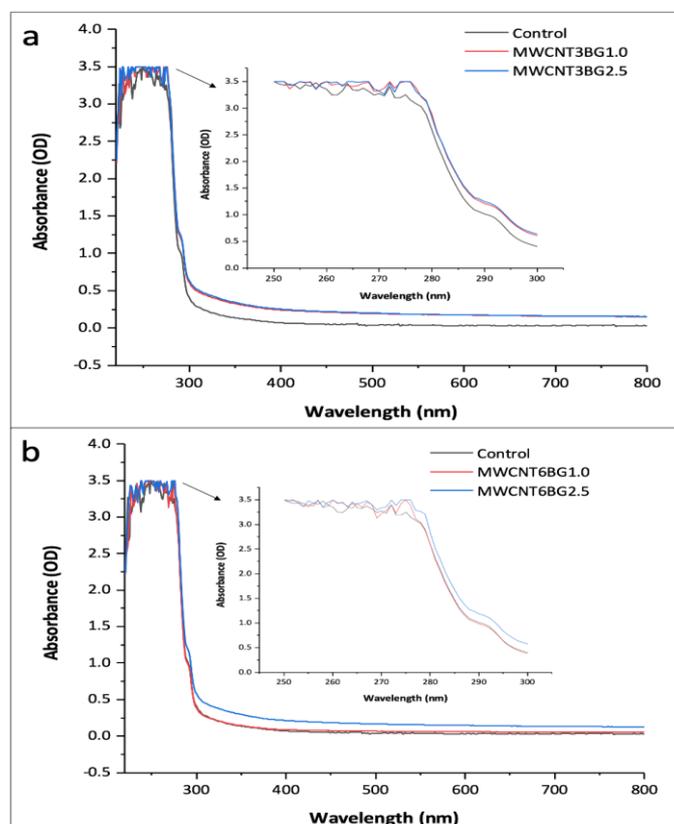
As for graphene-BG suspensions, Figure 4 demonstrates that absorbance intensity increases proportionally to the concentration of the material: the highest intensity being graphite (6 wt%) and BG powder (2.5 wt%) as shown in Figure 4b. This shows the complimentary relationship between both materials with enhancement of absorbance intensity after addition of BG. Furthermore, the results illustrate a stable exfoliation of graphene with almost the same values in absorbance intensity recorded similarly to Figure 1 which indicates no signs of agglomeration at even higher concentration of graphite as it is assumed that addition of BG also plays an important role in enhancing the solubility feature of graphene in chloroform- this being a vital characteristic in any physiological application.



**Fig. 4.** Absorbance intensity of liquid exfoliated graphene-BG suspension in chloroform. Different weight percentages of graphite (G) and BG used for comparisons as shown in a) 3 wt% of G exfoliated with 1.0 and 2.5 wt% of BG respectively and b) 6 wt% of G exfoliated with 1.0 and 2.5 wt% of BG respectively. Insert figures show respective clearer plateau absorption region ranging from 250-300 nm.

### 3.5 Exfoliation of MWCNT/BG suspension in chloroform

On the other hand, Figure 5 shown a trend which displays further agglomeration drawbacks of MWCNTs at higher concentration. MWCNTs shown the most stable state and higher intensity at weight percentage of 3 wt% with addition of 2.5 wt% BG, in contrast to higher concentration of MWCNTs as depicted in Figure 5a and 5b. As comparison to Figure 2, a drop in absorbance intensity values can be seen for all concentrations of MWCNTs, even after incorporation of BG, which might be due to either further agglomerations of both particles or due to dominant of lower absorbance intensity values possessed by BG upon addition to MWCNTs. The drawback is seen to somehow hinder the processing ability of these two prominent materials.



**Fig. 5.** Absorbance intensity of different weight percentage of MWCNT-BG suspension in chloroform as shown in a) 3 wt% of MWCNT exfoliated with 1.0 and 2.5 wt% of BG respectively and b) 6 wt% of MWCNT exfoliated with 1.0 and 2.5 wt% of BG respectively. Insert figures show respective clearer plateau absorption region ranging from 250-300 nm.

## 4 Conclusions

To conclude, a comparative absorbance intensity study between exfoliation of graphene and MWCNT respectively, with addition of BG in chloroform has been discussed. Graphene demonstrates greater stability and composition upon the liquid exfoliation in chloroform which is further enhanced on addition of BG as compared to MWCNTs. This characteristic is crucial as to illustrate the complimentary relationship between both types of materials- corresponding to their solubility profile which in terms affects, for example, the ability of cell adhesion on contact with physiological fluid. In contrast, MWCNTs demonstrate an inverse relationship in agglomeration effects before and after addition of BG, which may cause limitations in the preparation and processing of materials especially in key, surface-dependent, applications such as biomedical engineering therapies.

Future studies following on from the current findings where further characterisations, for example analysing morphology and composition of the composite materials, are highly anticipated. These observations are vital in confirming the synthesized materials and also to extend into biological study which will further evaluate the functionality of BG in facilitating and enhancing the overall composite, especially with graphene.

### Conflict of interest

The authors declare no conflict of interests.

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